PATENT ABSTRACTS OF JAPAN

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(54) THERMAL RECORDING MATERIAL

(57)Abstract:
PURPOSE: To obtain a thermal recording material improved in plasticizer resistance, water resistance, thermal background color development resistance and head matching properties by an epoxy type crosslinking agent.
CONSTITUTION: In a thermal recording material wherein a thermal recording layer forming a color by heat is provided on a support and a protective layer based on a resin and a crosslinking agent is further provided on the thermal recording layer, a condensate of glycol polyglycidyl ether and an epoxy type crosslinking agent containing a benzene ring having glycidyl ether or ester at its land 4-positions is used as the crosslinking agent. Further, a back coat layer containing the condensate is provided to the rear of the support.

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CLAIMS

[Claim(s)]
[Claim 1] The thermal recording ingredient characterized by containing the condensate of glycol poly glycidyl ether and the epoxy system cross linking agent containing the benzene ring which has glycidyl ether or ester in the 1 or 4th place as this cross linking agent in the thermal recording ingredient which prepares the heat-sensitive recording layer which carries out coloration with heat on a base material, and comes further to prepare the protective layer which uses resin and a cross linking agent as a principal component on this heat-sensitive recording layer.
[Claim 2] The thermal recording ingredient characterized by preparing the heat-sensitive recording layer which carries out coloration with heat on a base material, and preparing the back coat layer which makes a condensate with the epoxy system cross linking agent containing the benzene ring which has glycidyl ether or ester in a base material rear face at glycol poly glycidyl ether and the 1 or 4th place a cross linking agent, and uses this and resin as a principal component.
[Claim 3] glycol poly glycidyl ether and the epoxy system cross linking agent containing the benzene ring which has glycidyl ether or ester in the 1 or 4th place — weight — the thermal recording ingredient according to claim 1 or 2 characterized by using the product which carried out the condensation reaction with the mixing ratio 1 / 10 - 10/1 as a cross linking agent.

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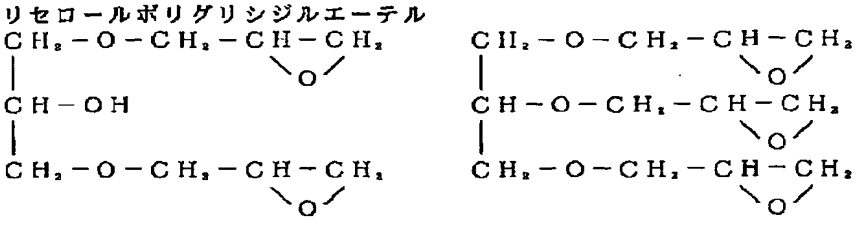
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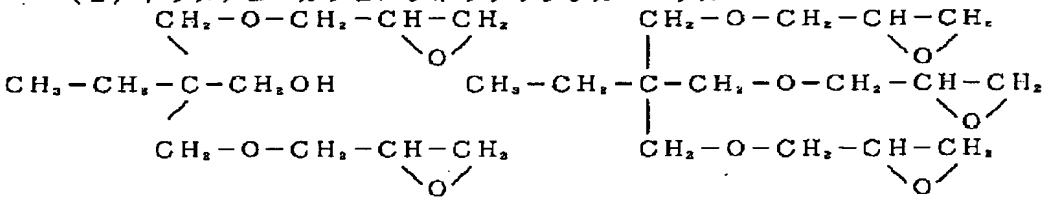
DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the thermal recording ingredient excellent in plasticizer-proof nature etc.
[0002]
[Description of the Prior Art] A coloring image is obtained by heating the thermal recording ingredient which prepared the sensible-heat layer which uses as a principal component the compound which consists of acid which carries out coloration of the leuco color to for example, a leuco color with heat on base materials, such as paper and a film, with a heat head, heat-stylus laser light, a stroboscope lamp, etc.
[0003] This kind of thermal recording ingredient has actuation complicated to record, and unnecessary equipment compared with other record ingredients, and since it is moreover recordable in a short time, it is used as various record ingredients, such as facsimile, a ticket machine, a computer, and a recorder label.
[0004] However, the fault that an image will disappear if plasticizers, such as ODA and DOP, are contacted, or the white section colors this thermal recording ingredient with solvents, such as ethanol and ethyl acetate, or it is inferior to image dependability exists.
[0005] Then, preparing a protective layer on a heat-sensitive recording layer as an approach of these-improving is proposed (refer to JP,54-128347,A and JP,54-3594,A). In order to raise oilproof and plasticizer-proof nature to such a protective layer, the proposal that water soluble resin, for example, polyvinyl alcohol, the denaturation type and starch, its denaturation type, etc. are effective is also made (refer to JP,56-126193,A and JP,56-13793,A).
[0006] However, the protective layer using such water soluble resin lacks a water resisting property in many cases, and the method (JP,57-188392,A) of stiffening a protective layer by using a cross linking agent together is used well. Although what was excellent in many things being proposed as this cross linking agent, for example, using a glycidyl system cross linking agent (referring to JP,57-188392,A) at oilproof and matching-proof nature (dregs antisticking to a heat head) is obtained, a water resisting property cannot say reactivity with it being enough well, either.
[0007] Moreover, although excelled in the water resisting property and the chemical-proof, since the protective layer (refer to JP,64-61287,A) which used the griot KISHIRU system cross linking agent for the amino compound generates formalin, it is unsuitable to use of a food-grade label. Furthermore, about the cross linking agent containing the amino group, yellowing of a protective layer is caused, the aziridine system cross linking agent is stable in a water solution, and problems, such as generating of formalin, are left behind about the glycidyl amine system cross linking agent. Although use of an epoxy system cross linking agent is proposed by JP,49-36343,A and JP,60-68990,A, a glycol type thing has a natural complexion coloring problem by heat. Furthermore, although the problem of heat-resistant natural complexion coloring does not have the epoxy system cross linking agent which has glycidyl ether or ester in the 1 or 4th place of the benzene ring, its reactivity is weak and inferior to a water resisting property in it. And according to concomitant use of these two kinds of epoxy system cross linking agents, although a certain amount of [heat-resistant natural complexion color enhancement and a water resisting property] improvement is accepted, it is still inadequate.
[0008]
[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the thermal recording ingredient excellent in a water resisting property, heat-resistant natural complexion coloring, and head matching nature as well as plasticizer-proof nature by amelioration of the above-mentioned epoxy system cross linking agent.
[0009]
[Means for Solving the Problem] This invention is characterized by using the compound to which condensation of the epoxy system cross linking agent which has glycidyl ether or ester in the protective layer further prepared on the heat-sensitive recording layer which carries out coloration with the heat formed on the base material, or the back coat layer on the rear face of a base material as this cross linking agent in resin and the thermal recording ingredient which made the cross linking agent contain at the 1 or 4th place of glycol poly glycidyl ether and the benzene ring was carried out. The thermal recording ingredient which fitted the above-mentioned purpose by this is offered. In addition, the thermal recording ingredient of this invention does not interfere, even when an under coat layer is prepared between a base material and a sensible-heat coloring layer.
[0010] The cross linking agents used for this invention are the mixed weight ratio 1 / 10 - 10/1, and the epoxy system compound preferably condensed in 3 / 10 - 7/1 about the epoxy system resin which has glycidyl ether or ester in the 1 or 4th place of (a) glycol poly glycidyl ether and (b) benzene ring as a simple substance. Although the following are mentioned as an example of a simple substance, it is not limited to these.
[0011] (a) Glycol poly glycidyl ether

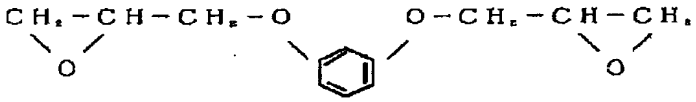
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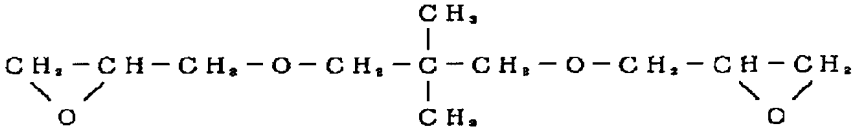
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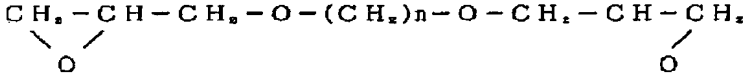
（３）レゾルシンジグリシジルエーテル



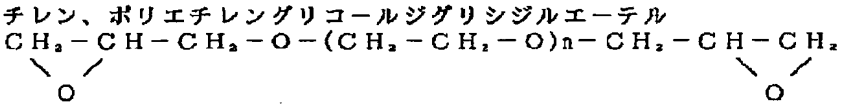
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（５）１，６－ヘキサンジオールジグリシジルエーテル



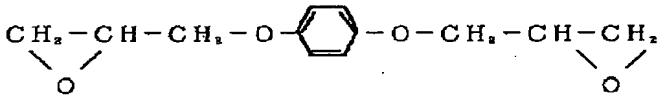
（６）エチレン、ポリエチレングリコールジグリシジルエーテル



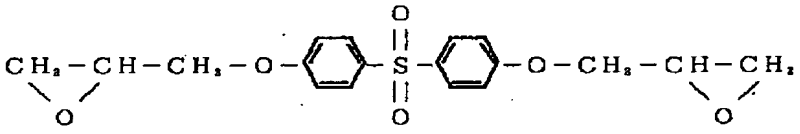
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[0012] (b) The epoxy system cross linking agent which has glycidyl ether or ester in the 1 or 4th place of the benzene ring

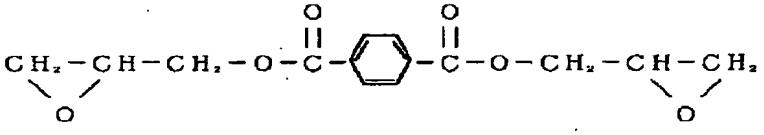
（１）ハイドロキノンジグリシジルエーテル



（２）ビスフェノールＳジグリシジルエーテル



（３）テレフタル酸ジグリシジルエーテル



[0013] Moreover, in this invention, concomitant use with epoxy system cross linking agents other than the polyamide epichlorohydrin system and boric-acid aziridine which are conventionally used with the epoxy system cross linking agent of above-mentioned this invention, a glycidyl amine, glyoxal, a methylol radical content compound, and the epoxy system cross linking agent used for the condensation reaction of this invention can also be performed.

[0014] As resin used for a protective layer (henceforth an overcoat layer), and a back coat layer For example, polyvinyl alcohol, a cellulosic, starch, and its derivative, Cull POKISHIRU radical denaturation polyvinyl alcohol, polyacrylic acid, and its derivative, Styrene / acrylic-acid copolymer and its derivative, the Pori (meta) acrylamides, and those derivatives, Styrene / acrylic acid / acrylamide copolymer, amino-group denaturation polyvinyl alcohol, Epoxy denaturation polyvinyl alcohol, polyethyleneimine, aquosity polyester, Water soluble resin, such as aquosity polyurethane, an isobutylene / maleic-anhydride copolymer, and its derivative, Although polyester, polyurethane, an acrylic ester system (**) polymer, styrene / acrylic copolymer, an epoxy resin, polyvinyl acetate, a polyvinylidene chloride, polyvinyl chlorides, and these derivatives are mentioned, water soluble resin is desirable especially.

[0015] Moreover, in an overcoat layer and a back coat layer, the well-known auxiliary addition component used from the former other than the above resin/cross linking agent, for example, a filler, a surfactant, the heat fusibility matter (or lubricant), a pressure coloring inhibitor, etc. can be used together. In this case, as a filler, the impalpable powder of organic systems, such as urea-HORIMARIN resin besides inorganic system impalpable powder, such as a calcium carbonate, a silica, a zinc oxide, titanium oxide, an aluminum hydroxide, zinc hydroxide, a barium sulfate, clay, talc, calcium by which surface preparation was carried out, and a silica, styrene / methacrylic-acid copolymer, and polystyrene resin, can be mentioned, for example. Moreover, as heat fusibility matter, a thing with the melting point with an extent [, such as a heat fusibility organic compound of condensate / of various waxes besides a higher fatty acid or its ester, an amide, or a metal salt aromatic carboxylic acid, and an amine /, benzoic-acid phenyl ester, high-class straight chain glycol, 3, 4-epoxy-hexahydrophthalic acid dialkyl, high-class ketone, and P-benzyl biphenyl and others,] of 50-200 degrees C is mentioned.

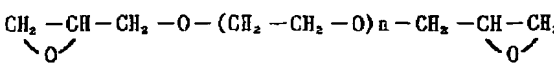
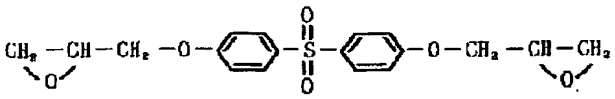
[0016] Although there are a thing using the coloring reaction of a leuco color and a developer, a thing using the reaction of a diazo compound and a coupler, a thing using the reaction of isocyanate and an amine, etc. as a method which carries out coloration with heat in this invention, especially a coloring method is not limited. Here, explanation is advanced about the method using a general leuco color.

[0017] Although two or more sorts use it, mixing, as such a leuco color, the leuco color used in this invention being independent or the thing applied to this kind of thermofax is used for arbitration, for example, the leuco compound of colors, such as a triphenylmethane color system, a fluoran system, a phenothiazin system, an auramine system, and a SUPIRO pyran system, is used preferably. As an example of such a leuco color, a thing as shown below is mentioned, for example. 3 and 3-screw (p-dimethylamino phenyl)-phthalide, 3, and 3-screw (p-dimethylamino phenyl)-6-dimethylamino phthalide (alias name crystal violet lactone), 3 and 3-screw (p-dimethylamino phenyl)-6-diethylamino phthalide, 3 and 3-screw (p-dimethylamino phenyl)-6-chloro phthalide, 3 and 3-screw (p-dibutylamino phenyl) phthalide, 3-cyclo HEKISHIARU amino-6-chlorofluoran, 3-dimethylamino -5, 7-dimethyl fluoran, 3-N-methyl-N-isobutyl-6-methyl-7-anilinofluoran, 3-N-ethyl-N-amyl-6-methyl-7-anilinofluoran, 3-diethylamino-7-chlorofluoran, 3-diethylamino-7-methyl fluoran, 3-diethylamino -7, 8-bends fluoran, 3-diethylamino-6-methyl-7-chlorofluoran, 3-(N-p-tolyl-N-ethylamino)-6-methyl-7-anilinofluoran, 3-pyrrolidino-6-methyl-7-anilinofluoran, 2-[N-(3'-trifluormethyl phenyl) amino]-6-diethylamino fluoran, 2-[3, 6-screw (diethylamino)-9-(o-chloroanilino) xanthyl benzoic-acid lactam], 3-diethylamino-6-methyl-7-(m-TORIKURUROMECHIRUANIRINO) fluoran, 3-diethylamino-7-(o-chloroanilino) fluoran, 3-dibutylamino-7-(o-chloroanilino) fluoran, 3-N-methyl - N-amyl amino-6-methyl-7-anilinofluoran, 3-N-methyl-N-cyclohexylamino-6-methyl-7-anilinofluoran, 3-diethylamino-6-methyl-7-anilinofluoran, 3-diethylamino-6-methyl-7-(2', 4'-dimethyl ANIRINO) fluoran, 3-(N and N-diethylamino)-5-methyl-7-(N and N-dibenzylamino) fluoran, Benzoyl leuco methylene blue, a 6 '- chloro -8'-methoxy-benzoin DORINO-pilus loss pyran, A 6 '- BUROMO -3'-methoxy-benzoin DORINO-pilus loss pyran, 3-(2'- hydroxy-4'-dimethylamino phenyl)-3-(2 '- methoxy - 5'-chlorophenyl) phthalide, 3-(2'- hydroxy-4'-dimethylamino phenyl)-3-(2 '- methoxy -5'-nitrophenyl) phthalide, 3-(2'- hydroxy-4'-diethylaminophenyl)-3-(2 '- methoxy -5'-methylphenyl) phthalide, 3-(2 '- methoxy -4'-dimethylamino phenyl)-3-(2'-hydroxy-4 '-chloro -5'-methylphenyl) phthalide, 3-morpholino-7-(N-propyl-trifluoromethyl ANIRINO) fluoran, 3-pyrrolidino-7-trifluoromethyl anilinofluoran, 3-diethylamino-5-chloro-7-(N-benzyl-trifluoromethyl ANIRINO) fluoran, 3-pyrrolidino-7-(G p-chlorophenyl) methylamino fluoran, 3-diethylamino-5-chloro-7-(alpha-phenyl ethylamino) fluoran, 3-(N-ethyl-p-torr IJINO)-7-(alpha-phenyl ethylamino) fluoran, 3-diethylamino-7-(o-methoxycarbonyl phenylamino) fluoran, 3-diethylamino-5-methyl-7-(alpha-phenyl ethylamino) fluoran, 3-diethylamino-7-piperidino fluoran, 2-chloro-3-(N-methyl torr IJINO)-7-(p-n-butylanilino) fluoran, 3-(N-methyl-N-isopropylamino)-6-methyl-7-anilinofluoran, 3-dibutylamino-6-methyl-7-anilinofluoran, 3, 6-screw (dimethylamino) fluorene SUPIRO (9 3')-6-dimethylamino phthalide, 3-(N-benzyl-N-cyclohexylamino)-5.6-benzo - 7-alpha-naphthyl amino-4'-BUROMO fluoran, 3-diethylamino-6-chloro-7-anilinofluoran, 3-N-ethyl-N - Amino (2-ethoxy propyl)-6-methyl-7-anilinofluoran, 3-N-ethyl - N-tetrahydrofurfuryl amino-6-methyl-7-anilinofluoran, 3-diethylamino-6-methyl-7-MESHICHIJINO - 4', 5'-benzo fluoran, etc.

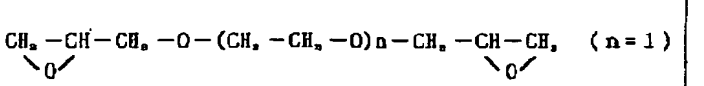
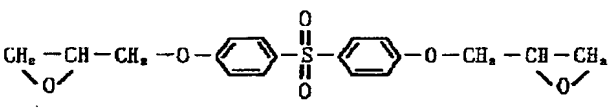
[0018] Moreover, as a developer used by this invention, a compound, for example, the phenol nature compound, a thiophenol nature compound, a thiourea derivative, a various organic acid, its various metal salt, etc. of the electronic receptiveness which makes said leuco color color at the time of contact are applied preferably, and a thing as shown below as the example is mentioned. A - isopropylidene bisphenol, and 4 and 4 '4, 4'-isopropylidene screw (o-methyl phenol), 4, a 4 '- secondary butylidenebis phenols 4 and 4'-isopropylidene screw (2-tertiary butylphenol), A - cyclohexylidene diphenol, and 4 and 4 '4, 4'-isopropylidene screw (2-chlorophenol), 2 and 2'-methylenebis (4-methyl-6-tertiary butylphenol), 2 and 2'-methylenebis (4-ethyl-6-tertiary butylphenol), 4 and 4'-butylidenebis (6-tertiary butyl-2-methyl phenol), 1, 1, 3-tris (2-methyl-4-hydroxy-5-tertiary buthylphenyl) butane, 1 and 1, 3-tris (2-methyl-4-hydroxy-5-cyclohexyl phenyl) butane, 4, and 4'-thio screw (6-tertiary butyl-2-methyl phenol)
4, 4 '- diphenol sulfone and 4-isopropoxy -4'-hydroxy diphenylsulfone, A - hydroxy diphenylsulfone, and 4-benzyloxy-4'4, 4'-diphenol sulfoxide, P-hydroxybenzoic-acid isopropyl, P-hydroxybenzoic-acid benzyl, Protocatechuic-acid benzyl, gallic-acid stearyl, gallic-acid lauryl, Gallic-acid octyl, 1, 7-screw (4-hydroxy phenylthio) -3, 5-dioxa heptane, 1, 5-screw (4-hydroxy phenylthio) -3-OKISA pentane, 1, a 3-screw (4-hydroxy phenylthio)-propane, 1, a 3-screw (4-hydroxy phenylthio)-2-hydroxy propane, - diphenyl thiourea, and N'N, N'-JI (m-chlorophenyl) thiourea, [N, and] The salicylanilide, the 5-chloro-salicylanilide, a 2-hydroxy-3-naphthoic acid, A 1-hydroxy-1-naphthoic acid, a 1-hydroxy-2-naphthoic acid, Metal salts, such as zinc of a hydroxy naphthoic acid, aluminum, and calcium, Screw-(4-hydroxyphenyl) acetic-acid methyl ester, screw-(4-hydroxyphenyl) benzyl-acetate ester, 1, 3-screw (4-hydroxy cumyl) benzene, 1, 4-screw (4-hydroxy cumyl) benzene, 2, a 4'-diphenol sulfone, 3, 3'-diaryl -4, a 4'-diphenol sulfone, alpha and alpha-screw (4-hydroxyphenyl)-alpha-methyl toluene, the antipyrin complex of thiocyanic acid zinc, tetrabromobisphenol A, the tetrabromo bisphenol S, etc.

[0019] In this invention, in order to carry out joint support of said leuco color, a developer, and the auxiliary component on a base material, the various binders of common use can be used suitably. For example, polyvinyl alcohol, starch and its derivative, a methoxy cellulose, Hydroxyethyl cellulose, a carboxymethyl cellulose, methyl cellulose, Cellulosics, such as ethyl cellulose, sodium

polyacrylate, A polyvinyl pyrrolidone, acrylamide / acrylic ester copolymer, Acrylamide / acrylic ester / methacrylic-acid ternary polymerization object, Styrene / maleic-anhydride copolymer alkali salt, an isobutylene / maleic-anhydride copolymer alkali salt, Others [water soluble polymers /, such as polyacrylamide, sodium alginate gelatin, and casein,], Latexes, such as an emulsion of polyvinyl acetate, polyurethane, polyacrylic ester, poly metallyl acid ester, a vinyl chloride / vinyl acetate copolymer, and an ethylene / vinyl acetate copolymer, and styrene / butadiene / acrylic copolymer, etc. are mentioned.
[0020] Moreover, in this invention, the auxiliary addition component commonly used further by this kind of thermal recording ingredient with said leuco color, a developer, and an auxiliary component if needed, for example, a loading material, a surfactant, etc. can be used together. In this case, as a loading material, the impalpable powder of organic systems, such as urea-formalin resin besides inorganic system impalpable powder, such as a calcium carbonate, a silica, a zinc oxide, titanium oxide, an aluminum hydroxide, zinc hydroxide, a barium sulfate, clay, talc, calcium by which surface preparation was carried out, and a silica, styrene / methacrylic-acid copolymer, and polystyrene resin, can be mentioned, for example.
[0021] In addition, in this invention, the layer which contains a loading material, a binder, etc. as an under coat layer if needed can also be prepared between a base material and a heat-sensitive recording layer. In this case, what was illustrated in said heat-sensitive recording layer as an example of a loading material and a binder, and the same thing are mentioned.
[0022] It is also possible to carry out the laminating of the overcoat layer more than two-layer furthermore.
[0023] Although the thermal recording ingredient of this invention is used in various fields, it can use the stability of the outstanding above mentioned coloring image and the above mentioned outstanding natural complexion section especially, and can use it advantageously as a thermal recording mold label sheet and thermal recording mold MAG ticket paper. What is necessary is in the case of a thermal recording mold label sheet, to replace with this exfoliation pasteboard in the case of magnetic ticket paper, and just to prepare the magnetic-recording layer which uses a ferromagnetic and a binder as a principal component that what is necessary is to prepare the heat-sensitive recording layer containing the above mentioned leuco color and the above mentioned developer, and said protective layer in one field of a base material, and just to form exfoliation pasteboard in the field of another side of a base material through an adhesives layer.
[0024] [Example] An example explains this invention to a detail further. In addition, each the section and % which are shown below are weight criteria.
[0025]
(Formation of a heat-sensitive recording layer)
(A liquid)
3-(N-methyl-N-cyclohexyl) amino-6-methyl-7- The three sections Anilinofluoran Polyvinyl alcohol 10% water solution The ten sections Water The 80 sections (B liquid)
4-hydroxyphenyl-4'-isopropoxy phenyl sulfone The ten sections Calcium carbonate The ten sections 1, 1, 3-tris (2-methyl-4-hydroxy-5-cyclo HEKIRU phenyl) butane The five sections Polyvinyl alcohol 10% water solution The 20 sections Water By mixing each fraction liquid also with the 55 sections A and B each liquid after 24-hour distribution in a sand mill A:B=1:3, sensible-heat coloring layer coating liquid was obtained, and also it applied and dried so that the amount of desiccation might become 5 g/m2 in the basis-weight 50 g/m2 high-quality paper, and the paper applied [heat-sensitive recording layer] was obtained.
[0026]
(Formation of an overcoat layer)
(C fluid)
A kaolin The ten sections Polyvinyl alcohol 10% water solution The ten sections Water The 80 sections These were distributed in the sand mill for 15 hours, and kaolin dispersion liquid were obtained.
(D-K liquid)
D-K liquid was created during the next formula using the cross linking agent like Table 1 - a Table 2 publication.
Kaolin dispersion liquid The 30 sections Polyvinyl alcohol 10% water solution The three sections 10% water solution of cross linking agents (dispersion liquid) The six sections Water Spreading desiccation of the 34 section D-K liquid was respectively carried out so that dry weight might become 3 g/m2 in the sensible-heat coloring layer paint paper, and the paper applied [overcoat layer] was obtained respectively. Furthermore, surface treatment was performed in the supercalender and the sample of examples 1-3 and the examples 1-5 of a comparison was obtained.
[0027]
(Formation of a back coat layer)
(L, M liquid)
During the next formula, as shown in Table 3, L and M liquid were created using the cross linking agent.
Kaolin dispersion liquid The 20 sections Polyvinyl alcohol 10% water solution The 40 sections 10% water solution of cross linking agents The eight sections Water The calender after spreading desiccation performed surface treatment for L and M liquid respectively so that dry weight might become 3 g/m2 at the heat-sensitive recording layer of 42 section examples 2 and the example 1 of a comparison, and the rear face of the paper applied [overcoat layer], and the sample of an example 4 and the example 6 of a comparison was obtained.
[0028]
[Table 1]

	架　橋　剤	液
実施例１	エチレングリコールジグリシジルエーテル  （ｎ＝１） ビスフェノールＳジグリシジルエーテル  を重量混合比５：１０で脱水縮合した化合物 （分子量約１１００、軟化点５０℃付近）	D
実施例２	実施例１の架橋剤２種を重量混合比３：１０で脱水縮合した化合物 （分子量約１，１００、軟化点１００℃以上）	E
実施例３	実施例２の架橋剤２種を重量混合比３：１０で脱水縮合した化合物 （分子量約３，３００、軟化点１００℃以上）	F

[0029]
[Table 2]

	架　橋　剤	液
比較例１	グリオキザール	G
比較例２	エチレングリコールジグリシジルエーテル 	H
比較例３	ビスフェノールＳジグリシジルエーテル 	I
比較例４	実施例１の架橋剤の２種の混合 （重量比５：１０）	J
比較例５	実施例１の架橋剤の２種の混合 （重量比３：１０）	K

[0030]
[Table 3]

	架　橋　剤	液
実施例４	実施例２に同じ	L
比較例５	比較例１に同じ	M

[0031] The following evaluation trials were performed about the created thermal recording ingredient like the above. The result is shown in Table 4.
- A waterproof test (reactivity)
What dipped the sample underwater 16 hrs after 40 degrees C and 16hr neglect is rubbed with a finger, and separation is investigated.
- Carry out 70-degree-C1hr neglect of the heat-resistant natural complexion coloring test sample. The concentration before and behind the neglect is measured with the Macbeth concentration meter, and the degree of coloring of natural complexion is investigated.
- Perform the load of a 20-sheet pile and 3 kg/m2, and carry out 16hr neglect of the 40 degrees C of the blocking test samples. A subsequent sample comrade's adhesion degree is seen.
- Measure the concentration of spreading, 30 degrees C, and 16hr printing sections for the printing back DOA by heat block to the concentration of 1.30 with the Macbeth densimeter at a plasticizer-proof nature test sample, and see the degree of a discharge.
- See the degree of the dregs adhesion on an after [printing] head with the mileage of 10km in the printer which installed the matching nature test KYOCERA nature thermal head.
[0032]
[Table 4]

		耐水性	耐熱地肌、発色	ブロッキング性	耐可塑剤	ヘッドマチング性
オーバーコート	実施例1	○	0.12 (○)	−	1.27	○
	実施例2	○	0.16 (○)	−	1.26	○
	実施例3	○	0.14 (○)	−	1.21	○
	比較例1	△	0.21 (△)	−	1.02	×
	比較例2	○	0.45 (×)	−	1.24	○
	比較例3	×	0.10 (○)	−	1.23	△
	比較例4	△	0.25 (△)	−	1.21	△
	比較例5	△	0.35 (×)	−	1.21	△
バックコート	実施例4	○	−	○	−	−
	比較例6	△	−	×	−	−

[0033] − Water resisting property O:HAKURI−less **: Those with **** HAKURI x: They are completely HAKURI and heat−resistant natural complexion coloring. O:good **: **** is good. x: A defect and head matching nature O:good **: **** is good. x: A defect and blocking nature O: That of HAGASU does not take the force (immediately or automatically HAGARERU).
x: That of HAGASU takes the force.
[0034]
[Effect of the Invention] The thermal recording ingredient which was excellent in the overcoat layer or back coat layer which uses resin and a cross linking agent as a principal component so that clearly from Table 4 as well as especially plasticizer−proof nature at a water resisting property, heat−resistant natural complexion coloring, blocking nature, and head matching nature by using the compound with an epoxy system cross linking agent with glycidyl ether or ester which carried out dehydration condensation as a cross linking agent for the 1 or 4th place of glycol poly glycidyl ether and the benzene ring is obtained.

[Translation done.]

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TECHNICAL FIELD

[Industrial Application] This invention relates to the thermal recording ingredient excellent in plasticizer-proof nature etc.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] A coloring image is obtained by heating the thermal recording ingredient which prepared the sensible-heat layer which uses as a principal component the compound which consists of acid which carries out coloration of the leuco color to for example, a leuco color with heat on base materials, such as paper and a film, with a heat head, heat-stylus laser light, a stroboscope lamp, etc.

[0003] This kind of thermal recording ingredient has actuation complicated to record, and unnecessary equipment compared with other record ingredients, and since it is moreover recordable in a short time, it is used as various record ingredients, such as facsimile, a ticket machine, a computer, and a recorder label.

[0004] However, the fault that an image will disappear if plasticizers, such as ODA and DOP, are contacted, or the white section colors this thermal recording ingredient with solvents, such as ethanol and ethyl acetate, or it is inferior to image dependability exists.

[0005] Then, preparing a protective layer on a heat-sensitive recording layer as an approach of these-improving is proposed (refer to JP,54-128347,A and JP,54-3594,A). In order to raise oilproof and plasticizer-proof nature to such a protective layer, the proposal that water soluble resin, for example, polyvinyl alcohol, the denaturation type and starch, its denaturation type, etc. are effective is also made (refer to JP,56-126193,A and JP,56-13793,A).

[0006] However, the protective layer using such water soluble resin lacks a water resisting property in many cases, and the method (JP,57-188392,A) of stiffening a protective layer by using a cross linking agent together is used well. Although what was excellent in many things being proposed as this cross linking agent, for example, using a glycidyl system cross linking agent (referring to JP,57-188392,A) at oilproof and matching-proof nature (dregs antisticking to a heat head) is obtained, a water resisting property cannot say reactivity with it being enough well, either.

[0007] Moreover, although excelled in the water resisting property and the chemical-proof, since the protective layer (refer to JP,64-61287,A) which used the griot KISHIRU system cross linking agent for the amino compound generates formalin, it is unsuitable to use of a food-grade label. Furthermore, about the cross linking agent containing the amino group, yellowing of a protective layer is caused, the aziridine system cross linking agent is stable in a water solution, and problems, such as generating of formalin, are left behind about the glycidyl amine system cross linking agent. Although use of an epoxy system cross linking agent is proposed by JP,49-36343,A and JP,60-68990,A, a glycol type thing has a natural complexion coloring problem by heat. Furthermore, although the problem of heat-resistant natural complexion coloring does not have the epoxy system cross linking agent which has glycidyl ether or ester in the 1 or 4th place of the benzene ring, its reactivity is weak and inferior to a water resisting property in it. And according to concomitant use of these two kinds of epoxy system cross linking agents, although a certain amount of [heat-resistant natural complexion color enhancement and a water resisting property] improvement is accepted, it is still inadequate.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention] The thermal recording ingredient which was excellent in the overcoat layer or back coat layer which uses resin and a cross linking agent as a principal component so that clearly from Table 4 as well as especially plasticizer-proof nature at a water resisting property, heat-resistant natural complexion coloring, blocking nature, and head matching nature by using the compound with an epoxy system cross linking agent with glycidyl ether or ester which carried out dehydration condensation as a cross linking agent for the 1 or 4th place of glycol poly glycidyl ether and the benzene ring is obtained.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the thermal recording ingredient excellent in a water resisting property, heat-resistant natural complexion coloring, and head matching nature as well as plasticizer-proof nature by amelioration of the above-mentioned epoxy system cross linking agent.

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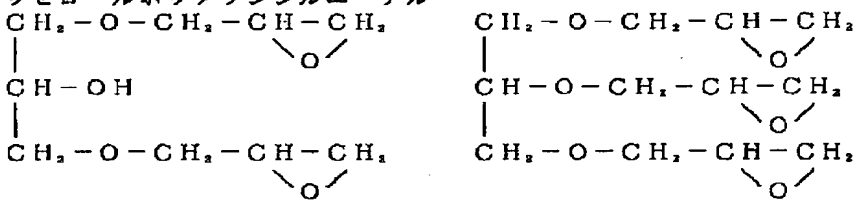
MEANS

[Means for Solving the Problem] This invention is characterized by using the compound to which condensation of the epoxy system cross linking agent which has glycidyl ether or ester in the protective layer further prepared on the heat-sensitive recording layer which carries out coloration with the heat formed on the base material, or the back coat layer on the rear face of a base material as this cross linking agent in resin and the thermal recording ingredient which made the cross linking agent contain at the 1 or 4th place of glycol poly glycidyl ether and the benzene ring was carried out. The thermal recording ingredient which fitted the above-mentioned purpose by this is offered. In addition, the thermal recording ingredient of this invention does not interfere, even when an under coat layer is prepared between a base material and a sensible-heat coloring layer.

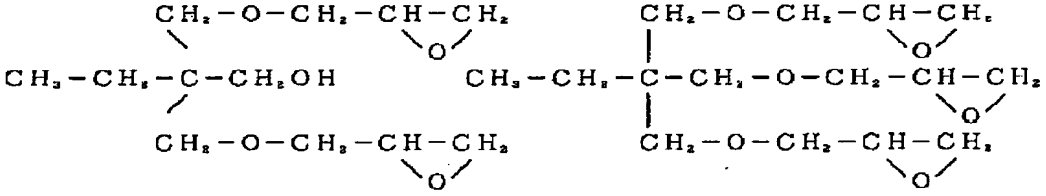
[0010] The cross linking agents used for this invention are the mixed weight ratio 1 / 10 - 10/1, and the epoxy system compound preferably condensed in 3 / 10 - 7/1 about the epoxy system resin which has glycidyl ether or ester in the 1 or 4th place of (a) glycol poly glycidyl ether and (b) benzene ring as a simple substance. Although the following are mentioned as an example of a simple substance, it is not limited to these.

[0011] (a) Glycol poly glycidyl ether

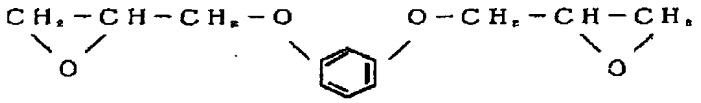
（１）グリセロールポリグリシジルエーテル



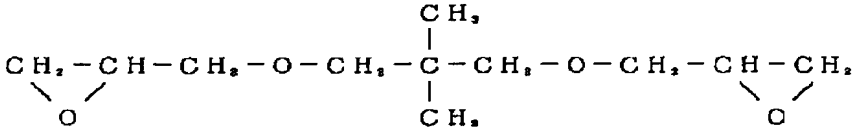
（２）トリメチロールプロパンポリグリシジルエーテル



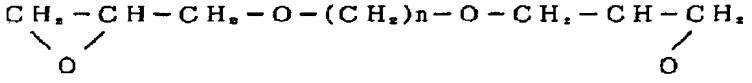
（３）レゾルシンジグリシジルエーテル



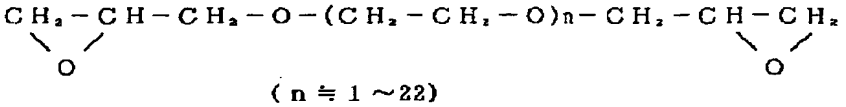
（４）ネオペンチルグリコールジグリシジルエーテル



（５）１，６－ヘキサンジオールジグリシジルエーテル



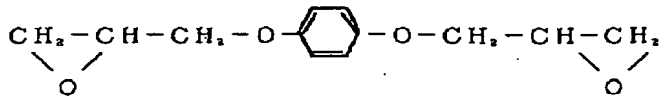
（６）エチレン、ポリエチレングリコールジグリシジルエーテル



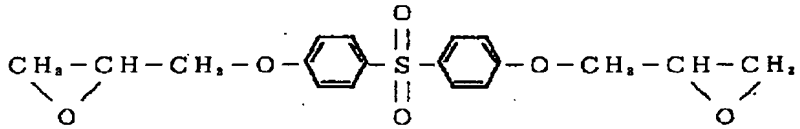
（ｎ≒１～22）

[0012] (b) The epoxy system cross linking agent which has glycidyl ether or ester in the 1 or 4th place of the benzene ring

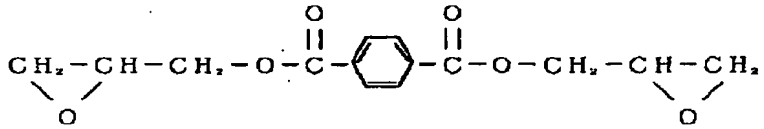
（１）ハイドロキノンジグリシジルエーテル



（２）ビスフェノールＳジグリシジルエーテル



（３）テレフタル酸ジグリシジルエーテル



[0013] Moreover, in this invention, concomitant use with epoxy system cross linking agents other than the polyamide epichlorohydrin system and boric-acid aziridine which are conventionally used with the epoxy system cross linking agent of above-mentioned this invention, a glycidyl amine, glyoxal, a methylol radical content compound, and the epoxy system cross linking agent used for the condensation reaction of this invention can also be performed.
[0014] As resin used for a protective layer (henceforth an overcoat layer), and a back coat layer For example, polyvinyl alcohol, a cellulosic, starch, and its derivative, Cull POKISHIRU radical denaturation polyvinyl alcohol, polyacrylic acid, and its derivative, Styrene / acrylic-acid copolymer and its derivative, the Pori (meta) acrylamides, and those derivatives, Styrene / acrylic acid / acrylamide copolymer, amino-group denaturation polyvinyl alcohol, Epoxy denaturation polyvinyl alcohol, polyethyleneimine, aquosity polyester, Water soluble resin, such as aquosity polyurethane, an isobutylene / maleic-anhydride copolymer, and its derivative, Although polyester, polyurethane, an acrylic ester system (**) polymer, styrene / acrylic copolymer, an epoxy resin, polyvinyl acetate, a polyvinylidene chloride, polyvinyl chlorides, and these derivatives are mentioned, water soluble resin is desirable especially.
[0015] Moreover, in an overcoat layer and a back coat layer, the well-known auxiliary addition component used from the former other than the above resin/cross linking agent, for example, a filler, a surfactant, the heat fusibility matter (or lubricant), a pressure coloring inhibitor, etc. can be used together. In this case, as a filler, the impalpable powder of organic systems, such as urea-HORIMARIN resin besides inorganic system impalpable powder, such as a calcium carbonate, a silica, a zinc oxide, titanium oxide, an aluminum hydroxide, zinc hydroxide, a barium sulfate, clay, talc, calcium by which surface preparation was carried out, and a silica, styrene / methacrylic-acid copolymer, and polystyrene resin, can be mentioned, for example. Moreover, as heat fusibility matter, a thing with the melting point with an extent [, such as a heat fusibility organic compound of condensate / of various waxes besides a higher fatty acid or its ester, an amide, or a metal salt aromatic carboxylic acid, and an amine /, benzoic-acid phenyl ester, high-class straight chain glycol, 3, 4-epoxy-hexahydrophthalic acid dialkyl, high-class ketone, and P-benzyl biphenyl and others,] of 50-200 degrees C is mentioned.
[0016] Although there are a thing using the coloring reaction of a leuco color and a developer, a thing using the reaction of a diazo compound and a coupler, a thing using the reaction of isocyanate and an amine, etc. as a method which carries out coloration with heat in this invention, especially a coloring method is not limited. Here, explanation is advanced about the method using a general leuco color.
[0017] Although two or more sorts use it, mixing, as such a leuco color, the leuco color used in this invention being independent or the thing applied to this kind of thermofax is used for arbitration, for example, the leuco compound of colors, such as a triphenylmethane color system, a fluoran system, a phenothiazin system, an auramine system, and a SUPIRO pyran system, is used preferably. As an example of such a leuco color, a thing as shown below is mentioned, for example. 3 and 3-screw (p-dimethylamino phenyl)-phthalide, 3, and 3-screw (p-dimethylamino phenyl)-6-dimethylamino phthalide (alias name crystal violet lactone), 3 and 3-screw (p-dimethylamino phenyl)-6-diethylamino phthalide, 3 and 3-screw (p-dimethylamino phenyl)-6-chloro phthalide, 3 and 3-screw (p-dibutylamino phenyl) phthalide, 3-cyclo HEKISHIARU amino-6-chlorofluoran, 3-dimethylamino -5, 7-dimethyl fluoran, 3-N-methyl-N-isobutyl-6-methyl-7-anilinofluoran, 3-N-ethyl-N-amyl-6-methyl-7-anilinofluoran, 3-diethylamino-7-chlorofluoran, 3-diethylamino-7-methyl fluoran, 3-diethylamino -7, 8-bends fluoran, 3-diethylamino-6-methyl-7-chlorofluoran, 3-(N-p-tolyl-N-ethylamino)-6-methyl-7-anilinofluoran, 3-pyrrolidino-6-methyl-7-anilinofluoran, 2-[N-(3'-trifluormethyl phenyl) amino]-6-diethylamino fluoran, 2-[3, 6-screw (diethylamino)-9-(o-chloroanilino) xanthyl benzoic-acid lactam], 3-diethylamino-6-methyl-7-(m-TORIKURUROMECHIRUANIRINO) fluoran, 3-diethylamino-7-(o-chloroanilino) fluoran, 3-dibutylamino-7-(o-chloroanilino) fluoran, 3-N-methyl - N-amyl amino-6-methyl-7-anilinofluoran, 3-N-methyl-N-cyclohexylamino-6-methyl-7-anilinofluoran, 3-diethylamino-6-methyl-7-anilinofluoran, 3-diethylamino-6-methyl-7-(2', 4'-dimethyl ANIRINO) fluoran, 3-(N and N-diethylamino)-5-methyl-7-(N and N-dibenzylamino) fluoran, Benzoyl leuco methylene blue, a 6 '- chloro -8'-methoxy-benzoin DORINO-pilus loss pyran, A 6 '- BUROMO -3'-methoxy-benzoin DORINO-pilus loss pyran, 3-(2'- hydroxy-4'-dimethylamino phenyl)-3-(2 '- methoxy -5'-chlorophenyl) phthalide, 3-(2'- hydroxy-4'-dimethylamino phenyl)-3-(2 '- methoxy -5'-nitrophenyl) phthalide, 3-(2'- hydroxy-4'-diethylaminophenyl)-3-(2 '- methoxy -5'-methylphenyl) phthalide, 3-(2 '- methoxy -4'-dimethylamino phenyl)-3-(2'-hydroxy-4 '-chloro -5'-methylphenyl) phthalide, 3-morpholino-7-(N-propyl-trifluoromethyl ANIRINO) fluoran, 3-pyrrolidino-7-trifluoromethyl anilinofluoran, 3-diethylamino-5-chloro-7-(N-benzyl-trifluoromethyl ANIRINO) fluoran, 3-pyrrolidino-7-(G p-chlorophenyl) methylamino fluoran, 3-diethylamino-5-chloro-7-(alpha-phenyl ethylamino) fluoran, 3-(N-ethyl-p-torr IJINO)-7-(alpha-phenyl ethylamino) fluoran, 3-diethylamino-7-(o-methoxycarbonyl phenylamino) fluoran, 3-diethylamino-5-methyl-7-(alpha-phenyl ethylamino) fluoran, 3-diethylamino-7-piperidino fluoran, 2-chloro-3-(N-methyl torr IJINO)-7-(p-n-butylanilino) fluoran, 3-(N-

methyl-N-isopropylamino)-6-methyl-7-anilinofluoran, 3-dibutylamino-6-methyl-7-anilinofluoran, 3, 6-screw (dimethylamino) fluorene SUPIRO (9 3')-6-dimethylamino phthalide, 3-(N-benzyl-N-cyclohexylamino)-5.6-benzo - 7-alpha-naphthyl amino-4'-BUROMO fluoran, 3-diethylamino-6-chloro-7-anilinofluoran, 3-N-ethyl-N - Amino (2-ethoxy propyl)-6-methyl-7-anilinofluoran, 3-N-ethyl - N-tetrahydrofurfuryl amino-6-methyl-7-anilinofluoran, 3-diethylamino-6-methyl-7-MESHICHIJINO - 4', 5'-benzo fluoran, etc.

[0018] Moreover, as a developer used by this invention, a compound, for example, the phenol nature compound, a thiophenol nature compound, a thiourea derivative, a various organic acid, its various metal salt, etc. of the electronic receptiveness which makes said leuco color color at the time of contact are applied preferably, and a thing as shown below as the example is mentioned. A - isopropylidene bisphenol, and 4 and 4 '4, 4'-isopropylidene screw (o-methyl phenol), 4, a 4 '- secondary butylidenebis phenols 4 and 4'-isopropylidene screw (2-tertiary butylphenol), A - cyclohexylidene diphenol, and 4 and 4 '4, 4'-isopropylidene screw (2-chlorophenol), 2 and 2'-methylenebis (4-methyl-6-tertiary butylphenol), 2 and 2'-methylenebis (4-ethyl-6-tertiary butylphenol), 4 and 4'-butylidenebis (6-tertiary butyl-2-methyl phenol), 1, 1, 3-tris (2-methyl-4-hydroxy-5-tertiary buthylphenyl) butane, 1 and 1, 3-tris (2-methyl-4-hydroxy-5-cyclohexyl phenyl) butane, 4, and 4'-thio screw (6-tertiary butyl-2-methyl phenol)
4, 4 '- diphenol sulfone and 4-isopropoxy -4'-hydroxy diphenylsulfone, A - hydroxy diphenylsulfone, and 4-benzyloxy-4'4, 4'-diphenol sulfoxide, P-hydroxybenzoic-acid isopropyl, P-hydroxybenzoic-acid benzyl, Protocatechuic-acid benzyl, gallic-acid stearyl, gallic-acid lauryl, Gallic-acid octyl, 1, 7-screw (4-hydroxy phenylthio) -3, 5-dioxa heptane, 1, 5-screw (4-hydroxy phenylthio) -3-OKISA pentane, 1, a 3-screw (4-hydroxy phenylthio)-propane, 1, a 3-screw (4-hydroxy phenylthio)-2-hydroxy propane, - diphenyl thiourea, and N'N, N'-JI (m-chlorophenyl) thiourea, [N, and] The salicylanilide, the 5-chloro-salicylanilide, a 2-hydroxy-3-naphthoic acid, A 1-hydroxy-1-naphthoic acid, a 1-hydroxy-2-naphthoic acid, Metal salts, such as zinc of a hydroxy naphthoic acid, aluminum, and calcium, Screw-(4-hydroxyphenyl) acetic-acid methyl ester, screw-(4-hydroxyphenyl) benzyl-acetate ester, 1, 3-screw (4-hydroxy cumyl) benzene, 1, 4-screw (4-hydroxy cumyl) benzene, 2, a 4'-diphenol sulfone, 3, 3'-diaryl -4, a 4'-diphenol sulfone, alpha and alpha-screw (4-hydroxyphenyl)-alpha-methyl toluene, the antipyrin complex of thiocyanic acid zinc, tetrabromobisphenol A, the tetrabromo bisphenol S, etc.

[0019] In this invention, in order to carry out joint support of said leuco color, a developer, and the auxiliary component on a base material, the various binders of common use can be used suitably. For example, polyvinyl alcohol, starch and its derivative, a methoxy cellulose, Hydroxyethyl cellulose, a carboxymethyl cellulose, methyl cellulose, Cellulosics, such as ethyl cellulose, sodium polyacrylate, A polyvinyl pyrrolidone, acrylamide / acrylic ester copolymer, Acrylamide / acrylic ester / methacrylic-acid ternary polymerization object, Styrene / maleic-anhydride copolymer alkali salt, an isobutylene / maleic-anhydride copolymer alkali salt, Others [water soluble polymers /, such as polyacrylamide, sodium alginate gelatin, and casein,], Latexes, such as an emulsion of polyvinyl acetate, polyurethane, polyacrylic ester, poly metallyl acid ester, a vinyl chloride / vinyl acetate copolymer, and an ethylene / vinyl acetate copolymer, and styrene / butadiene / acrylic copolymer, etc. are mentioned.

[0020] Moreover, in this invention, the auxiliary addition component commonly used further by this kind of thermal recording ingredient with said leuco color, a developer, and an auxiliary component if needed, for example, a loading material, a surfactant, etc. can be used together. In this case, as a loading material, the impalpable powder of organic systems, such as urea-formalin resin besides inorganic system impalpable powder, such as a calcium carbonate, a silica, a zinc oxide, titanium oxide, an aluminum hydroxide, zinc hydroxide, a barium sulfate, clay, talc, calcium by which surface preparation was carried out, and a silica, styrene / methacrylic-acid copolymer, and polystyrene resin, can be mentioned, for example.

[0021] In addition, in this invention, the layer which contains a loading material, a binder, etc. as an under coat layer if needed can also be prepared between a base material and a heat-sensitive recording layer. In this case, what was illustrated in said heat-sensitive recording layer as an example of a loading material and a binder, and the same thing are mentioned.

[0022] It is also possible to carry out the laminating of the overcoat layer more than two-layer furthermore.

[0023] Although the thermal recording ingredient of this invention is used in various fields, it can use the stability of the outstanding above mentioned coloring image and the above mentioned outstanding natural complexion section especially, and can use it advantageously as a thermal recording mold label sheet and thermal recording mold MAG ticket paper. What is necessary is in the case of a thermal recording mold label sheet, to replace with this exfoliation pasteboard in the case of magnetic ticket paper, and just to prepare the magnetic-recording layer which uses a ferromagnetic and a binder as a principal component that what is necessary is to prepare the heat-sensitive recording layer containing the above mentioned leuco color and the above mentioned developer, and said protective layer in one field of a base material, and just to form exfoliation pasteboard in the field of another side of a base material through an adhesives layer.

[Translation done.]

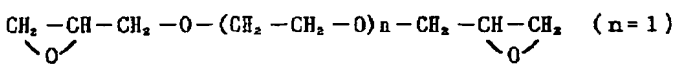
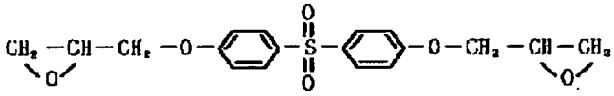
* NOTICES *

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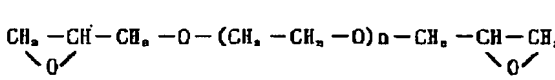
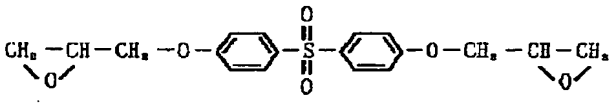
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

EXAMPLE

[Example] An example explains this invention to a detail further. In addition, each the section and % which are shown below are weight criteria.
[0025]
(Formation of a heat-sensitive recording layer)
(A liquid)
3-(N-methyl-N-cyclohexyl) amino-6-methyl-7- The three sections Anilinofluoran Polyvinyl alcohol 10% water solution The ten sections Water The 80 sections (B liquid)
4-hydroxyphenyl-4'-isopropoxy phenyl sulfone The ten sections Calcium carbonate The ten sections 1, 1, 3-tris (2-methyl-4-hydroxy-5-cyclo HEKIRU phenyl) butane The five sections Polyvinyl alcohol 10% water solution The 20 sections Water Each fraction liquid is mixed also with the 55 sections A and B each liquid after 24-hour distribution in a sand mill A:B=1:3. Sensible-heat coloring layer coating liquid was obtained, and also it applied and dried so that the amount of desiccation might become 5 g/m2 in the basis-weight 50 g/m2 high-quality paper, and the paper applied [heat-sensitive recording layer] was obtained.
[0026]
(Formation of an overcoat layer)
(C fluid)
Kaolin The ten sections Polyvinyl alcohol 10% water solution The ten sections Water The 80 sections These It distributed in the sand mill for 15 hours, and kaolin dispersion liquid were obtained.
(D-K liquid)
D-K liquid was created during the next formula using the cross linking agent like Table 1 - a Table 2 publication.
Kaolin dispersion liquid The 30 sections Polyvinyl alcohol 10% water solution The three sections 10% water solution of cross linking agents (dispersion liquid) The six sections Water It sets [in the sensible-heat coloring layer paint paper / dry weight] to 3g/m2 in 34 section D-K liquid and needs. Spreading desiccation was carried out respectively and the paper applied [overcoat layer] was obtained respectively. Furthermore, surface treatment was performed in the supercalender and the sample of examples 1-3 and the examples 1-5 of a comparison was obtained.
[0027]
(Formation of a back coat layer)
(L, M liquid)
During the next formula, as shown in Table 3, L and M liquid were created using the cross linking agent.
Kaolin dispersion liquid The 20 sections Polyvinyl alcohol 10% water solution The 40 sections 10% water solution of cross linking agents The eight sections Water They are L and M liquid so that dry weight may become 3 g/m2 at the heat-sensitive recording layer of 42 section examples 2 and the example 1 of a comparison, and the rear face of the paper applied [overcoat layer]. The calender after spreading desiccation performed surface treatment respectively, and the sample of an example 4 and the example 6 of a comparison was obtained.
[0028]
[Table 1]

	架　橋　剤	液
実施例１	エチレングリコールジグリシジルエーテル  （ｎ＝１） ビスフェノールＳジグリシジルエーテル  を重量混合比５：１０で脱水縮合した化合物 （分子量約１１００、軟化点５０℃付近）	D
実施例２	実施例１の架橋剤２種を重量混合比３：１０で脱水縮合した化合物 （分子量約１，１００、軟化点１００℃以上）	E
実施例３	実施例２の架橋剤２種を重量混合比３：１０で脱水縮合した化合物 （分子量約３，３００、軟化点１００℃以上）	F

[0029]
[Table 2]

	架　橋　剤	液
比較例１	グリオキザール	G
比較例２	エチレングリコールジグリシジルエーテル 	H
比較例３	ビスフェノールＳジグリシジルエーテル 	I
比較例４	実施例１の架橋剤の２種の混合 （重量比５：１０）	J
比較例５	実施例１の架橋剤の２種の混合 （重量比３：１０）	K

[0030]
[Table 3]

	架　橋　剤	液
実施例４	実施例２に同じ	L
比較例６	比較例１に同じ	M

[0031] The following evaluation trials were performed about the created thermal recording ingredient like the above. The result is shown in Table 4.
- A waterproof test (reactivity)
What dipped the sample underwater 16 hrs after 40 degrees C and 16hr neglect is rubbed with a finger, and separation is investigated.
- Carry out 70-degree-C1hr neglect of the heat-resistant natural complexion coloring test sample. The concentration before and behind the neglect is measured with the Macbeth concentration meter, and the degree of coloring of natural complexion is investigated.
- Perform the load of a 20-sheet pile and 3 kg/m2, and carry out 16hr neglect of the 40 degrees C of the blocking test samples. A subsequent sample comrade's adhesion degree is seen.
- Measure the concentration of spreading, 30 degrees C, and 16hr printing sections for the printing back DOA by heat block to the concentration of 1.30 with the Macbeth densimeter at a plasticizer-proof nature test sample, and see the degree of a discharge.
- See the degree of the dregs adhesion on an after [printing] head with the mileage of 10km in the printer which installed the matching nature test KYOCERA nature thermal head.
[0032]
[Table 4]

		耐水性	耐熱地肌、発色	ブロッキング性	耐可塑剤	ヘッドマチング性
オーバーコート	実施例1	○	0.12 (○)	−	1.27	○
	実施例2	○	0.16 (○)	−	1.26	○
	実施例3	○	0.14 (○)	−	1.21	○
	比較例1	△	0.21 (△)	−	1.02	×
	比較例2	○	0.45 (×)	−	1.24	○
	比較例3	×	0.10 (○)	−	1.23	△
	比較例4	△	0.25 (△)	−	1.21	△
	比較例5	△	0.35 (×)	−	1.21	△
バックコート	実施例4	○	−	○	−	−
	比較例6	△	−	×	−	−

[0033] − Water resisting property O:HAKURI−less **: Those with **** HAKURI x: They are completely HAKURI and heat−resistant natural complexion coloring. O:good **: **** is good. x: A defect and head matching nature O:good **: **** is good. x: A defect and blocking nature O: That of HAGASU does not take the force (immediately or automatically HAGARERU).
x: That of HAGASU takes the force.

[Translation done.]

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B41M 5/26					
		6956-2H	B41M 5/18	101 E	

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(54)【発明の名称】感熱記録材料

(57)【要約】
【目的】　エポキシ系架橋剤により耐可塑剤性、耐水性、耐熱地肌発色及びヘッドマッチング性の改良された感熱記録材料を得る。
【構成】　支持体上に熱により呈色する感熱記録層を設け、更に感熱記録層上に樹脂と架橋剤を主成分とする保護層を設けてなる感熱記録材料において、該架橋剤としてグリコールポリグリシジルエーテルと１，４位にグリシジルエーテルまたはエステルをもつベンゼン環を含むエポキシ系架橋剤との縮合物を含有させる。また支持体裏面に該縮合物を含有するバックコート層を設ける。

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【特許請求の範囲】

【請求項１】　支持体上に熱により呈色する感熱記録層を設け、更に該感熱記録層上に樹脂と架橋剤を主成分とする保護層を設けてなる感熱記録材料において、該架橋剤としてグリコールポリグリシジルエーテルと１，４位にグリシジルエーテルまたはエステルをもつベンゼン環を含むエポキシ系架橋剤との縮合物を含有することを特徴とする感熱記録材料。

【請求項２】　支持体上に熱により呈色する感熱記録層を設け、支持体裏面にグリコールポリグリシジルエーテルと１，４位にグリシジルエーテルまたはエステルをもつベンゼン環を含むエポキシ系架橋剤との縮合物を架橋剤とし、これと樹脂を主成分とするバックコート層を設けることを特徴とする感熱記録材料。

【請求項３】　グリコールポリグリシジルエーテルと１，４位にグリシジルエーテルまたはエステルをもつベンゼン環を含むエポキシ系架橋剤とを重量混合比で1/10～10/1で縮合反応させた生成物を架橋剤として用いることを特徴とする請求項１又は２記載の感熱記録材料。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は耐可塑剤性等に優れた感熱記録材料に関する。

【０００２】

【従来の技術】紙、フィルム等の支持体上に、例えばロイコ染料と熱によりロイコ染料を呈色させる酸性物質からなる化合物を主成分とする感熱層を設けた感熱記録材料は、熱ヘッド・熱ペン・レーザー光・ストロボランプ等で加熱することにより発色画像が得られる。

【０００３】この種の感熱記録材料は、他の記録材料に比べ、記録に煩雑な操作、装置が不要で、しかも短時間で記録できるため、ファクシミリ・券売機・電子計算機・レコーダー・ラベル等多方面の記録材料として用いられる。

【０００４】しかしながら該感熱記録材料はＯＤＡやＤＯＰ等の可塑剤に接触すると画像が消失したり、エタノール、酢酸エチル等の溶剤により白色部が発色したり、画像信頼性に劣るという欠点が存在する。

【０００５】そこでこれら改善する方法として感熱記録層上に保護層を設けることが提案されている（特開昭54-128347号、特開昭54-3594号公報参照）。このような保護層には耐油性、耐可塑剤性を高めるために水溶性樹脂、例えばポリビニルアルコールとその変性タイプ、デンプンとその変性タイプ等が有効であるという提案もなされている（特開昭56-126193、特開昭56-13793号公報参照）。

【０００６】しかし、このような水溶性樹脂を用いた保護層は、耐水性が欠ける場合が多く、架橋剤を併用することで保護層を硬化させる方法（特開昭57-188392号）がよく用いられている。該架橋剤としては多くのものが提案され、例えばグリシジル系架橋剤（特開昭57-188392号公報参照）を用いることで耐油性、耐マッチング性（熱ヘッドへのカス付着防止）に優れたものが得られているが、反応性がよくなく、耐水性も充分とはいえない。

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【０００７】またアミノ化合物にグリオキシル系架橋剤を使用した保護層（特開昭64-61287号公報参照）は、耐水性、耐薬品に優れているが、ホルマリンを発生するので食品用ラベルの使用には不適である。更にアミノ基を含む架橋剤に関しては、保護層の黄変を引き起し、アジリジン系架橋剤は水溶液中で安定であり、グリシジルアミン系架橋剤に関してはホルマリンの発生等の問題が残されている。特開昭49-36343号、特開昭60-68990号公報にはエポキシ系架橋剤の使用が提案されているが、グリコールタイプのものは熱による地肌発色問題がある。更にベンゼン環の１，４位にグリシジルエーテルまたはエステルを持つエポキシ系架橋剤は耐熱地肌発色の問題はないものの、反応性が弱く、耐水性に劣る。そしてこれら２種類のエポキシ系架橋剤の併用によれば耐熱地肌発色性及び耐水性はある程度の改善は認められるがまだまだ不充分である。

【０００８】

【発明が解決しようとする課題】本発明の目的は、上記エポキシ系架橋剤の改良により、耐可塑剤性はもちろん、耐水性、耐熱地肌発色、ヘッドマッチング性に優れた感熱記録材料を提供することにある。

【０００９】

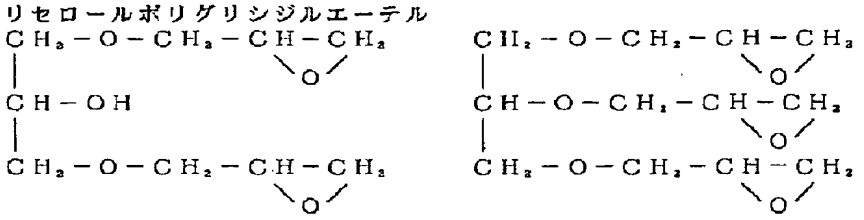
【課題を解決するための手段】本発明は、支持体上に設けた熱により呈色する感熱記録層の上に更に設けた保護層あるいは支持体裏面のバックコート層に、樹脂と架橋剤を含有させた感熱記録材料において、該架橋剤としてグリコールポリグリシジルエーテルとベンゼン環の１，４位にグリシジルエーテル又はエステルをもつエポキシ系架橋剤を縮合させた化合物を用いることを特徴とする。これにより上記目的に適した感熱記録材料が提供される。なお、本発明の感熱記録材料は、支持体と感熱発色層の間にアンダーコート層を設けた場合でも差支えない。

【００１０】本発明に使用する架橋剤は単体として（ａ）グリコールポリグリシジルエーテルと（ｂ）ベンゼン環の１，４位にグリシジルエーテルまたはエステルをもつエポキシ系樹脂を混合重量比率１／１０～１０／１、好ましくは３／１０～７／１で縮合したエポキシ系化合物である。単体の例としては次のものが挙げられるがこれらに限定されるものではない。

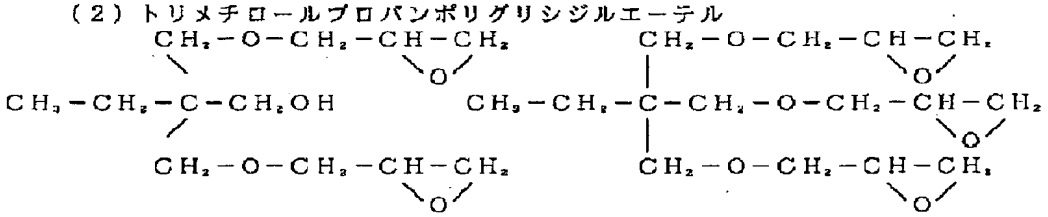
【００１１】（ａ）グリコールポリグリシジルエーテル

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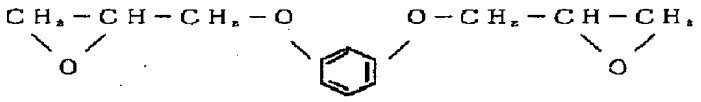
（１）グリセロールポリグリシジルエーテル



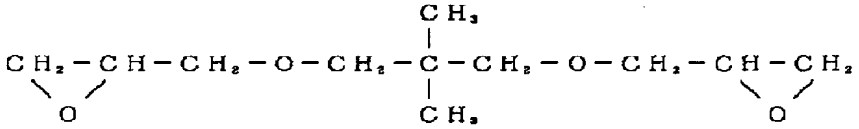
（２）トリメチロールプロパンポリグリシジルエーテル



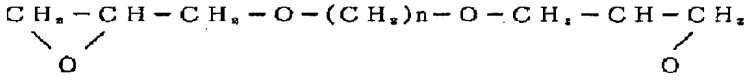
（３）レゾルシンジグリシジルエーテル



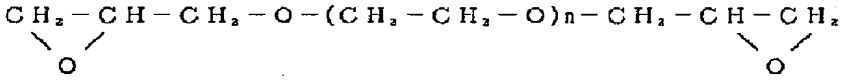
（４）ネオペンチルグリコールジグリシジルエーテル



（５）１，６－ヘキサンジオールジグリシジルエーテル



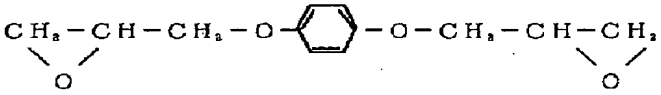
（６）エチレン、ポリエチレングリコールジグリシジルエーテル



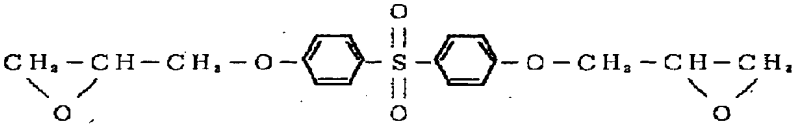
（ｎ≒１～22）

【００１２】（ｂ）ベンゼン環の１，４位にグリシジルエーテルまたはエステルをもつエポキシ系架橋剤

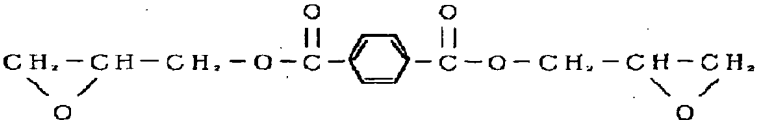
（１）ハイドロキノンジグリシジルエーテル



（２）ビスフェノールＳジグリシジルエーテル



（３）テレフタル酸ジグリシジルエーテル



【００１３】また本発明においては、上記本発明のエポキシ系架橋剤とともに従来より用いられているポリアミドエピクロルヒドリン系、ホウ酸アジリジン、グリシジルアミン、グリオキザール、メチロール基含有化合物、本発明の縮合反応に用いるエポキシ系架橋剤以外のエポキシ系架橋剤との併用も出来る。

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【００１４】保護層（以下オーバーコート層ともいう）及びバックコート層に用いる樹脂としては、例えばポリビニルアルコール、セルロース誘導体、デンプン及びその誘導体、カルボキシル基変性ポリビニルアルコール、ポリアクリル酸及びその誘導体、スチレン／アクリル酸共重合体及びその誘導体、ポリ（メタ）アクリルアミド及びそれらの誘導体、スチレン／アクリル酸／アクリルアミド共重合体、アミノ基変性ポリビニルアルコール、エポキシ変性ポリビニルアルコール、ポリエチレンイミン、水性ポリエステル、水性ポリウレタン、イソブチレン／無水マレイン酸共重合体及びその誘導体等の水溶性樹脂や、ポリエステル、ポリウレタン、アクリル酸エステル系（共）重合体、スチレン／アクリル系共重合体、エポキシ樹脂、ポリ酢酸ビニル、ポリ塩化ビニリデン、ポリ塩化ビニル及びこれらの誘導体が挙げられるが、中でも水溶性樹脂が好ましい。

【００１５】またオーバーコート層及びバックコート層には以上の樹脂／架橋剤の他に従来より用いられている公知の補助添加成分、例えば、フィラー、界面活性剤、熱可融性物質（又は滑剤）、圧力発色防止剤等を併用することができる。この場合、フィラーとしては、例えば、炭酸カルシウム、シリカ、酸化亜鉛、酸化チタン、水酸化アルミニウム、水酸化亜鉛、硫酸バリウム、クレー、タルク、表面処理されたカルシウムやシリカ等の無機系微粉末の他、尿素－ホリマリン樹脂、スチレン／メタクリル酸共重合体、ポリスチレン樹脂等の有機系の微粉末を挙げることができる。また熱可融性物質として、例えば、高級脂肪酸又はそのエステル、アミドもしくは金属塩の他、各種ワックス類、芳香族カルボン酸とアミンとの縮合物、安息香酸フェニルエステル、高級直鎖グリコール、3,4-エポキシ－ヘキサヒドロフタル酸ジアルキル、高級ケトン、P-ベンジルビフェニルその他の熱可融性有機化合物等の50～200℃の程度の融点を持つものが挙げられる。

【００１６】本発明において熱により呈色させる方式として、ロイコ染料と顕色剤との発色反応を利用するもの、ジアゾ化合物とカップラーの反応を利用するもの、イソシアナートとアミンの反応を利用するもの等があるが、特に発色方式は限定されるものではない。ここでは、一般的なロイコ染料を用いた方式について説明を進める。

【００１７】本発明において用いられるロイコ染料は単独又は２種以上混合して使用されるが、このようなロイコ染料としては、この種の感熱材料に適用されているものが任意に使用され、例えば、トリフェニルメタン系、フルオラン系、フェノチアジン系、オーラミン系、スピロピラン系等の染料のロイコ化合物が好ましく用いられる。このようなロイコ染料の具体例としては、例えば、以下に示すようなものが挙げられる。3，3－ビス（p－ジメチルアミノフェニル）－フタリド、3，3－ビス（p－ジメチルアミノフェニル）－6－ジメチルアミノフタリド（別名クリスタルバイオレットラクトン）、3，3－ビス（p－ジメチルアミノフェニル）－6－ジエチルアミノフタリド、3，3－ビス（p－ジメチルアミノフェニル）－6－クロロフタリド、3，3－ビス（p－ジブチルアミノフェニル）フタリド、3－シクロヘキシアルアミノ－6－クロロフルオラン、3－ジメチルアミノ－5，7－ジメチルフルオラン、3-N-メチル-N-イソブチル-6-メチル-7-アニリノフルオラン、3-N-エチル-N-アミル-6-メチル-7-アニリノフルオラン、3－ジエチルアミノ－7－クロロフルオラン、3－ジエチルアミノ－7－メチルフルオラン、3－ジエチルアミノ－7，8－ベンズフルオラン、3－ジエチルアミノ－6－メチル－7－クロロフルオラン、3－（N－p－トリル－N－エチルアミノ）－6－メチル－7－アニリノフルオラン、　3－ピロリジノ－6－メチル－7－アニリノフルオラン、2－｛N－（3'－トリフルオルメチルフエニル）アミノ｝－6－ジエチルアミノフルオラン、2－｛3，6－ビス（ジエチルアミノ）－9－(o－クロロアニリノ)キサンチル安息香酸ラクタム｝、3－ジエチルアミノ－6－メチル－7－（m－トリクロロメチルアニリノ）フルオラン、3－ジエチルアミノ－7－（o－クロロアニリノ）フルオラン、3－ジブチルアミノ－7－（o－クロロアニリノ）フルオラン、3－N－メチル－N－アミルアミノ－6－メチル－7－アニリノフルオラン、3－N－メチル－N－シクロヘキシルアミノ－6－メチル－7－アニリノフルオラン、3－ジエチルアミノ－6－メチル－7－アニリノフルオラン、3－ジエチルアミノ－6－メチル－7－（2'，4'-ジメチルアニリノ）フルオラン、3－（N，N－ジエチルアミノ）－5－メチル－7－（N，N－ジベンジルアミノ）フルオラン、ベンゾイルロイコメチレンブルー、6'－クロロ－8'－メトキシ－ベンゾインドリノ－ピリロスピラン、6'－ブロモ－3'－メトキシ－ベンゾインドリノ－ピリロスピラン、3－（2'－ヒドロキシ－4'－ジメチルアミノフェニル）－3－（2'－メトキシ－5'－クロロフエニル）フタリド、3－（2'－ヒドロキシ－4'－ジメチルアミノフェニル）－3－（2'－メトキシ－5'－ニトロフェニル）フタリド、3－（2'－ヒドロキシ－4'－ジエチルアミノフェニル）－3－（2'－メトキシ－5'－メチルフェニル）フタリド、3－（2'－メトキシ－4'－ジメチルアミノフェニル）－3－（2'－ヒドロキシ－4'－クロロ－5'－メチルフェニル）フタリド、3－モルホリノ－7－（N－プロピル－トリフルオロメチルアニリノ）フルオラン、3－ピロリジノ－7－トリフルオロメチルアニリノフルオラン、3－ジエチルアミノ－5－クロロ－7－（N－ベンジル－トリフルオロメチルアニリノ）フルオラン、3－ピロリジノ－7－（ジ－p－クロロフェニル）メチルアミノフルオラン、3－ジエチルアミノ－5－クロロ－7－（α－フェニルエチルアミノ）フルオラン、3－（N－エチル－p－トルイジノ）－7－（α－フェニルエチルアミノ）フルオラン、3－ジエ

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チルアミノ－7－（o－メトキシカルボニルフェニルアミノ）フルオラン、3－ジエチルアミノ－5－メチル－7－（α－フェニルエチルアミノ）フルオラン、3－ジエチルアミノ－7－ピペリジノフルオラン、2－クロロ－3－（N－メチルトルイジノ）－7－（p－n－ブチルアニリノ）フルオラン、3－（N-メチル-N-イソプロピルアミノ）-6-メチル-7-アニリノフルオラン、3－ジブチルアミノ－6－メチル－7－アニリノフルオラン、3,6－ビス（ジメチルアミノ）フルオレンスピロ(9,3')－6－ジメチルアミノフタリド、3－(N－ベンジル－N－シクロヘキシルアミノ）－5.6－ベンゾ－7－α－ナフチルアミノ－4'－ブロモフルオラン、3－ジエチルアミノ－6－クロロ－7－アニリノフルオラン、3-N-エチル-N-（2-エトキシプロピル)アミノ-6-メチル-7-アニリノフルオラン、3-N-エチル-N-テトラヒドロフルフリルアミノ-6-メチル-7-アニリノフルオラン、3－ジエチルアミノ－6－メチル－7－メシチジノ－4',5'－ベンゾフルオラン等。

【００１８】また本発明で用いる顕色剤としては、前記ロイコ染料を接触時発色させる電子受容性の種々の化合物、例えばフェノール性化合物、チオフェノール性化合物、チオ尿素誘導体、有機酸及びその金属塩等が好ましく適用され、その具体例としては以下に示すようなものが挙げられる。4,4'-イソプロピリデンビスフェノール、4,4'-イソプロピリデンビス（o-メチルフェノール）、4,4'-セカンダリーブチリデンビスフェノール 4,4'-イソプロピリデンビス（2-タ-シャリーブチルフェノール）、4,4'-シクロヘキシリデンジフェノール、4,4'-イソプロピリデンビス（2-クロロフェノール）、2,2'-メチレンビス（4-メチル-6-ターシャリーブチルフェノール）、2,2'-メチレンビス（4-エチル-6-ターシャリーブチルフェノール）、4,4'-ブチリデンビス（6-ターシャリーブチル-2-メチルフェノール）、1,1,3-トリス（2-メチル-4-ヒドロキシ-5-ターシャリブチルフェニル）ブタン、1,1,3-トリス（2-メチル-4-ヒドロキシ-5-シクロヘキシルフェニル）ブタン、4,4'-チオビス(6-ターシャリーブチル-2-メチルフェノール) 4,4'-ジフェノールスルホン、4-イソプロポキシ-4'-ヒドロキシジフェニルスルホン、4-ベンジロキシ-4'-ヒドロキシジフェニルスルホン、4,4'-ジフェノールスルホキシド、P-ヒドロキシ安息香酸イソプロピル、P-ヒドロキシ安息香酸ベンジル、プロトカテキユ酸ベンジル、没食子酸ステアリル、没食子酸ラウリル、没食子酸オクチル、1,7-ビス（4-ヒドロキシフェニルチオ）-3,5-ジオキサヘプタン、1,5-ビス（4-ヒドロキシフェニルチオ）-3-オキサペンタン、1,3-ビス（4-ヒドロキシフェニルチオ）-プロパン、1,3-ビス（4-ヒドロキシフェニルチオ）-2-ヒドロキシプロパン、N,N'-ジフェニルチオ尿素、N,N'-ジ（m-クロロフェニル）チオ尿素、サリチルアニリド、5-クロロ-サリチルアニリド、2-ヒドロキシ-3-ナフトエ酸、1-ヒドロキシ-1-ナフトエ酸、1-ヒドロキシ-2-ナフトエ酸、ヒドロキシナフトエ酸の亜鉛、アルミニウム、カルシウム等の金属塩、ビス-（4-ヒドロキシフェニル）酢酸メチルエステル、ビス-（4-ヒドロキシフェニル）酢酸ベンジルエステル、1,3-ビス（4-ヒドロキシクミル）ベンゼン、1,4-ビス（4-ヒドロキシクミル）ベンゼン、2,4'-ジフェノールスルホン、3,3'-ジアリル-4,4'-ジフェノールスルホン、α,α-ビス（4-ヒドロキシフェニル）-α-メチルトルエン、チオシアン酸亜鉛のアンチピリン錯体、テトラブロモビスフェノールA、テトラブロモビスフェノールS等。

【００１９】本発明においては、前記ロイコ染料、顕色剤及び補助成分を支持体上に結合支持させるために、慣用の種々の結合剤を適宜用いることができる。例えばポリビニルアルコール、澱粉及びその誘導体、メトキシセルロース、ヒドロキシエチルセルロース、カルボキシメチルセルロース、メチルセルロース、エチルセルロースなどのセルロース誘導体、ポリアクリル酸ソーダ、ポリビニルピロリドン、アクリルアミド／アクリル酸エステル共重合体、アクリルアミド／アクリル酸エステル／メタクリル酸三元共重合体、スチレン／無水マレイン酸共重合体アルカリ塩、イソブチレン／無水マレイン酸共重合体アルカリ塩、ポリアクリルアミド、アルギン酸ソーダ、ゼラチン、カゼイン等の水溶性高分子の他、ポリ酢酸ビニル、ポリウレタン、ポリアクリル酸エステル、ポリメタクリル酸エステル、塩化ビニル／酢酸ビニル共重合体、エチレン／酢酸ビニル共重合体のエマルジョンやスチレン／ブタジエン／アクリル系共重合体などのラテックス等が挙げられる。

【００２０】また、本発明においては、前記ロイコ染料及び顕色剤及び補助成分と共に、必要に応じ、更に、この種の感熱記録材料に慣用される補助添加成分、例えば、填料、界面活性剤等を併用することができる。この場合、填料としては、例えば炭酸カルシウム、シリカ、酸化亜鉛、酸化チタン、水酸化アルミニウム、水酸化亜鉛、硫酸バリウム、クレー、タルク、表面処理されたカルシウムやシリカ等の無機系微粉末の他、尿素－ホルマリン樹脂、スチレン／メタクリル酸共重合体、ポリスチレン樹脂などの有機系の微粉末を挙げることができる。

【００２１】なお、本発明においては、支持体と感熱記録層の間に、必要に応じアンダーコート層として填料、結合剤等を含有する層を設けることもできる。この場合、填料及び結合剤の具体例としては、前記感熱記録層において例示されたものと同様のものが挙げられる。

【００２２】さらにオーバーコート層を２層以上積層することも可能である。

【００２３】本発明の感熱記録材料は、種々の分野において利用されるが、殊に、前記した優れた発色画像及び地肌部の安定性を利用し、感熱記録型ラベルシートや、感熱記録型磁気券紙として有利に利用することができる。感熱記録型ラベルシートの場合、支持体の一方の面

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に、前記したロイコ染料及び顕色剤を含有する感熱記録層と前記保護層を設け、支持体の他方の面に、接着剤層を介して剥離台紙を設ければよく磁気券紙の場合は、この剥離台紙に代えて、強磁性体と結合剤とを主成分とする磁気記録層を設ければよい。

（感熱記録層の形成）

（Ａ液）

３－(Ｎ－メチル－Ｎ－シクロヘキシル)アミノ－６－メチル－７－アニリノフルオラン	3部
ポリビニルアルコール１０％水溶液	10部
水	80部

（Ｂ液）

４－ヒドロキシフェニル－４’－イソプロポキシフェニルスルホン	10部
炭酸カルシウム	10部
1,1,3-トリス(2-メチル-4-ヒドロキシ-5-シクロヘキルフェニル)ブタン	5部
ポリビニルアルコール１０％水溶液	20部
水	55部

Ａ、Ｂ各液ともサンドミルにて２４時間分散後、各分数液をＡ：Ｂ＝１：３にて混合することにより感熱発色層塗布液を得た、更に坪量50g/m²上質紙上に乾燥量が５g/m²になる様に塗布、乾燥し、感熱記録層塗布済紙を得た。

【００２６】

（オーバーコート層の形成）

（Ｃ液）

カオリン	10部
ポリビニルアルコール１０％水溶液	10部
水	80部

これらをサンドミルにて１５時間分散し、カオリン分散液を得た。

（Ｄ～Ｋ液）

次の処方中、架橋剤を表１～表２記載の如く用いてＤ～Ｋ液を作成した。

カオリン分散液	30部
ポリビニルアルコール１０％水溶液	3部
架橋剤１０％水溶液（分散液）	6部
水	34部

Ｄ～Ｋ液を感熱発色層塗布剤紙上に乾燥重量が３g/m²になるよう各々塗布乾燥し、オーバーコート層塗布済紙を各々得た。更にスーパーカレンダーにて表面処理を行い実施例１～３、比較例１～５のサンプルを得た。

【００２７】

（バックコート層の形成）

（Ｌ、Ｍ液）

次の処方中、架橋剤を表３の如く用いてＬ及びＭ液を作成した。

カオリン分散液	20部
ポリビニルアルコール１０％水溶液	40部
架橋剤１０％水溶液	8部
水	42部

実施例２及び比較例１の感熱記録層及びオーバーコート層塗布済紙の裏面に乾燥重量が３g/m²になるようにＬ、Ｍ液を各々塗布乾燥後キャレンダーで表面処理を行い、実施例４及び比較例６のサンプルを得た。

【００２８】

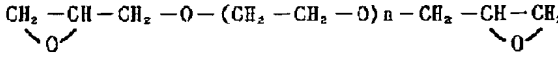
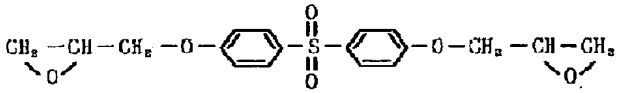
【表１】

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【００２４】〔実施例〕本発明を実施例により更に詳細に説明する。なお、以下で示す部及び％はいずれも重量基準である。

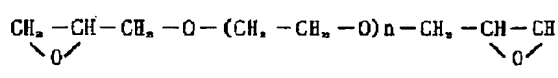
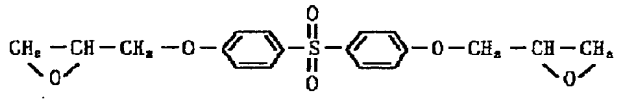
【００２５】

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	架　橋　剤	液
実施例１	エチレングリコールジグリシジルエーテル  （n＝１） ビスフェノールＳジグリシジルエーテル  を重量混合比５：１０で脱水縮合した化合物 （分子量約１１００、軟化点５０℃付近）	D
実施例２	実施例１の架橋剤２種を重量混合比３：１０で脱水縮合した化合物 （分子量約１，１００、軟化点１００℃以上）	E
実施例３	実施例２の架橋剤２種を重量混合比３：１０で脱水縮合した化合物 （分子量約３，３００、軟化点１００℃以上）	F

【００２９】　　【表２】

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	架　橋　剤	液
比較例１	グリオキザール	G
比較例２	エチレングリコールジグリシジルエーテル 	H
比較例３	ビスフェノールＳジグリシジルエーテル 	I
比較例４	実施例１の架橋剤の２種の混合 （重量比５：１０）	J
比較例５	実施例１の架橋剤の２種の混合 （重量比３：１０）	K

【００３０】

【表３】

	架　橋　剤	液
実施例４	実施例２に同じ	L
比較例５	比較例１に同じ	M

【００３１】上記の如く作成した感熱記録材料について以下の評価試験を行った。その結果を表４に示す。

・耐水性テスト（反応性）

サンプルを４０℃、１６ｈｒ放置後、水中に１６ｈｒ浸したものを指にてこすりハガレを調べる。

・耐熱地肌発色テスト

サンプルを７０℃１ｈｒ放置する。その放置前後の濃度をマクベス濃度計で測定し、地肌の発色の度合を調べる。

・ブロッキングテスト

サンプルを２０枚重ね、３kg/m²の加重を行い４０℃、１６ｈｒ放置する。その後のサンプル同志の付着度合をみる。

・耐可塑剤性テスト

サンプルにマクベス濃度計で１．３０の濃度に熱ブロックで印字後ＤＯＡを塗布、３０℃、１６ｈｒ印字部の濃度を測定し、消色の度合をみる。

・マッチング性テスト

京セラ性サーマルヘッドを設置した印字装置にて、走行距離１０Ｋｍで印字後ヘッド上のカス付着の度合をみる。

【００３２】

【表４】

		耐水性	耐熱地肌、発色	ブロッキング性	耐可塑剤	ヘッドマチング性
オーバーコート	実施例１	○	0.12 (○)	－	1.27	○
	実施例２	○	0.16 (○)	－	1.26	○
	実施例３	○	0.14 (○)	－	1.21	○
	比較例１	△	0.21 (△)	－	1.02	×
	比較例２	○	0.45 (×)	－	1.24	○
	比較例３	×	0.10 (○)	－	1.23	△
	比較例４	△	0.25 (△)	－	1.21	△
	比較例５	△	0.35 (×)	－	1.21	△
バックコート	実施例４	○	－	○	－	－
	比較例６	△	－	×	－	－

【００３３】・耐水性　　○：ハクリなし
△：やゝハクリあり　×：完全にハクリ
・耐熱地肌発色　　○：良好　　△：やゝ良好
×：不良
・ヘッドマッチング性　○：良好　　△：やゝ良好
×：不良
・ブロッキング性　　○：ハガスのに力を要しない（すぐ、又は自然にハガレル）
×：ハガスのに力を要する。

【００３４】【発明の効果】表４から明らかなように樹脂と架橋剤を主成分とするオーバーコート層あるいはバックコート層に、架橋剤として、グリコールポリグリシジルエーテルとベンゼン環の１，４位にグリシジルエーテルまたはエステルをもつエポキシ系架橋剤との脱水縮合した化合物を使用することにより耐可塑剤性はもちろん、特に耐水性、耐熱地肌発色、ブロッキング性、ヘッドマッチング性に優れた感熱記録材料が得られる。

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